

Linear aspects of the KKR formalism

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Abstract. We present one-dimensional KKR method with the aim to elucidate its linear features, particularly important in optimizing the numerical algorithms in energy bands computations. The conventional KKR equations based on the multiple scattering theory as well as novel forms of the secular matrix with nearly linear energy dependency of the eigenvalues are presented. The quasi-linear behaviour of these eigenvalue functions appears after (i) re-normalizing the wave functions in such a way that 'irregular' solutions vanish on the boundary of the 'muffin-tin' segments and (ii) integrating the full Green function over the whole Wigner-Seitz cell. In addition, using the aforementioned approach we derive one-dimensional analog of the generalized Lloyd formula.

The novel KKR approach illustrated in one-dimension can be almost directly applied to the higher dimensional cases. This should open prospects for the accurate KKR band structure computations of very complex materials.

1. Introduction

In the Korringa-Kohn-Rostoker (KKR) method the main problem in performing electronic structure calculations is due to strongly nonlinear dependence of the KKR-matrix eigenvalues on energy for a fixed k -point. It is very difficult to find properly all the zeros of eigenvalue functions, when there is a large number of atoms in the unit cell. Hence the fast and accurate extraction of all zeros of eigenvalues still remains a challenge in computation of complex materials.

Butler [1] and Schwitalla *et al.* [2] formulated the KKR formalism for one spatial dimension, which is very similar to its three-dimensional counterpart. The one-dimensional case is computationally much simpler and allows to formulate the substantial results in compact, analytical forms. Therefore, it is very attractive to investigate future of the KKR method along this line.

In this paper we use the Green function approach for solving the Schrödinger equation. As already known, the one-dimensional (1D) KKR method gives exact solutions. This is due to the facts that (i) the unit cell can be entirely filled by the non-overlapping (touching each other) 'muffin-tin' segments and (ii) the multipole expansion contains only two 'spherical harmonics' ($l = 0$ and $l = 1$). Furthermore, the KKR structure constants in the 1D case can be obtained analytically, which markedly facilitates numerical calculations.

Our paper is organized as follows. In Sec. 2 we recall after Butler [1] and Schwitalla *et al.* [2] the standard 1D-KKR formalism. In this section we also discuss few difficulties in determining the band structure in multi-atom systems if using the standard approach. Sec. 3 presents the novel form of the KKR-matrix in terms of logarithmic derivatives as well as the advantages of this approach with respect to the

standard KKR theory. Next, the generalized Lloyd formula [6] is derived, which helps in computation of the total number of states and placing properly the Fermi energy at early stage of calculations in real materials. In Sec. 5 we show illustrative results for an arbitrary chosen potential, which are followed by summary and conclusions (Sec. 6).

2. Standard KKR formalism in one dimension

We look for a solution of the 1D Schrödinger equation with Hamiltonian (atomic units are used, energy unit is 1 Ry):

$$H = -\frac{d^2}{dx^2} + V(x). \quad (1)$$

The potential in (1) is assumed to be translationally invariant with the period of lattice constant a , so it can be written as

$$V(x) = \sum_{n=-\infty}^{+\infty} v(x - na). \quad (2)$$

We assume $v(x)$ in (2) to vanish for $|x|$ greater than some radius S , and do not overlap each other. This assumption has the form analogous to the non-overlapping 'muffin-tin' potential in three-dimensional (3D) KKR theory. We shall expand the potential $v(x)$ in (2) and the wave functions around each center into symmetric and antisymmetric functions, analogous to the 3D expansion into the spherical harmonics. First, let us define 1D spherical coordinates centered at na -point,

$$x = \hat{x}r + na, \quad x \in \left[na - \frac{a}{2}, na + \frac{a}{2} \right], \quad (3)$$

with discrete directional coordinate, $\hat{x} = \text{sgn}(x)$, and radius $r \in [0, \frac{a}{2}]$. Then, with the definition of 1D analog of the spherical harmonics

$$Y_0(\hat{x}) = 1/\sqrt{2} \quad Y_1(\hat{x}) = \hat{x}/\sqrt{2}, \quad (4)$$

we decompose $v(x)$ into spherical and aspherical parts:

$$v(x) = \frac{1}{2}[v(r) + v(-r)] + \frac{\hat{x}}{2}[v(r) - v(-r)] = v_0(r)Y_0(\hat{x}) + v_1(r)Y_1(\hat{x}). \quad (5)$$

Similarly, we may write 1D multipole series for the wave function

$$\psi(x) = \psi_0(r)Y_0(\hat{x}) + \psi_1(r)Y_1(\hat{x}) \quad (6)$$

with the radial functions of the free Schrödinger equation given by the following regular

$$j_0(\sqrt{E}r) = \cos(\sqrt{E}r) \quad j_1(\sqrt{E}r) = \sin(\sqrt{E}r) \quad (7)$$

and 'irregular'

$$n_0(\sqrt{E}r) = \sin(\sqrt{E}r) \quad n_1(\sqrt{E}r) = -\cos(\sqrt{E}r) \quad (8)$$

special solutions. Also analogs of the 3D spherical Hankel functions, usually defined as $h_l(x) = j_l(x) + in_l(x)$, exist:

$$h_0(\sqrt{E}r) = \exp(i\sqrt{E}r) \quad h_1(\sqrt{E}r) = -i \exp(i\sqrt{E}r). \quad (9)$$

The square root \sqrt{E} is taken on the complex energy plane with the branch cut along the positive real axis. To proceed further we follow the steps in the multiple scattering formalism [8, 9], leading to the following form of the Bloch-Fourier Green's function

$$\begin{aligned} \langle x' | G(E, k) | x \rangle &= - \sum_l J_l(E, x_{>}) Z_l(E, x_{<}) \\ &+ \sum_{l', l} Z_{l'}(E, x') [t^{-1}(E) - B(E, k)]_{l'l}^{-1} Z_l(E, x) . \end{aligned} \quad (10)$$

In (10) $Z_l(E, x)$ and $J_l(E, x)$ are the regular and irregular solutions of the Schrödinger equation with the radial parts given in the asymptotic region ($r \geq S$) by

$$[Z(E, r)]_{l'l} = j_{l'}(\sqrt{E}r) [t^{-1}(E)]_{l'l} - \frac{i}{\sqrt{E}} h_{l'}(\sqrt{E}r) \delta_{l'l} \quad (11)$$

$$[J(E, r)]_{l'l} = j_{l'}(\sqrt{E}r) \delta_{l'l} . \quad (12)$$

$B(E, k)$ is the matrix of KKR structure constants with explicit form generalized to multi-atom case as given in Appendix. The matrix $t(E)$ is one-scatterer t -matrix and may be found from the wave functions

$$\psi_l(E, x) = \sum_{l'} Y_{l'}(\hat{x}) [\psi(E, r)]_{l'l} \quad (13)$$

with radial solutions satisfying the following set of differential equations

$$\frac{d^2}{dr^2} \psi(E, r) + [E - v(r)] \psi(E, r) = 0, \quad (14)$$

with the potential $v(r)$ in the matrix form

$$v(r) = \begin{bmatrix} v_s(r) & v_a(r) \\ v_a(r) & v_s(r) \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} v_0(r) & v_1(r) \\ v_1(r) & v_0(r) \end{bmatrix} . \quad (15)$$

The functions $\psi(E, r)$ are routinely available in computations starting at near origin ($r = 0$) with

$$[\psi(E, r)]_{l'l} = r^l \delta_{l'l} . \quad (16)$$

If in asymptotic region, for $r \geq S$, these radial functions behave as

$$[\psi(E, r)]_{l'l} = j_{l'}(\sqrt{E}r) [C(E)]_{l'l} - \frac{i}{\sqrt{E}} h_{l'}(\sqrt{E}r) [S(E)]_{l'l} \quad (17)$$

then

$$[C(E)]_{l'l} = W \left\{ [\psi(E, r)]_{l'l}, -\frac{i}{\sqrt{E}} h_{l'}(\sqrt{E}r) \right\}_{r=S}, \quad (18)$$

$$[S(E)]_{l'l} = W \left\{ j_{l'}(\sqrt{E}r), [\psi(E, r)]_{l'l} \right\}_{r=S} \quad (19)$$

with the Wronskian definition

$$W\{f, g\} = f \frac{\partial}{\partial r} g - g \frac{\partial}{\partial r} f. \quad (20)$$

Comparing (11) and (17) gives us the following relation for the t -matrix

$$t(E) = S(E) C^{-1}(E) . \quad (21)$$

The poles of GF in (10) determine energy dispersion curves in the form of bands. These poles are usually found from zeros of the KKR-determinant

$$\det |t^{-1}(E) - B(E, k)| = 0. \quad (22)$$

Furthermore, we define the matrix of logarithmic derivatives

$$D(E, r) = \frac{\partial}{\partial r} [\psi(E, r)] [\psi(E, r)]^{-1}. \quad (23)$$

The $D(E, r)$ matrix is not affected by changing of the regular solution normalization. Moreover, this matrix is symmetrical, i.e.

$$D^T(E, r) = D(E, r) \quad (24)$$

what can be proved by recalling that it satisfies equation of Ricatti type

$$\frac{\partial}{\partial r} D(E, r) + D^2(E, r) = v(r) - E \quad (25)$$

with the symmetrical potential matrix, $v^T(r) = v(r)$. At the 'muffin-tin' boundary point ($r = S$), we can simply write

$$D(E) = \frac{\partial}{\partial r} [\psi(E, r)] \Big|_{r=S} [\psi(E, S)]^{-1}. \quad (26)$$

The log-derivative matrix $D(E)$ is also directly related to the t -matrix by the following expression:

$$\begin{aligned} [v_P^{-1}(E)]_{\nu l} &= j_\nu(\sqrt{E}S) [t^{-1}(E)]_{\nu l} j_l(\sqrt{E}S) \\ &\quad - \frac{i}{\sqrt{E}} h_\nu(\sqrt{E}S) j_l(\sqrt{E}S) \delta_{\nu l} \end{aligned} \quad (27)$$

with the definition of the pseudopotential amplitude matrix

$$v_P^{-1}(E) = D(E) - D_0(E) \quad (28)$$

where

$$\begin{aligned} D_0(E) &= \frac{d}{dr} [j(\sqrt{E}r)] \Big|_{r=S} [j(\sqrt{E}S)]^{-1}, \\ [j(\sqrt{E}r)]_{\nu l} &= j_l(\sqrt{E}r) \delta_{\nu l}. \end{aligned} \quad (29)$$

3. Novel forms of the KKR-matrix in one dimension

In the standard KKR-methodology finding zeros of the matrix $[t^{-1}(E) - B(E, k)]$ in the GF formula (10) is central topic when computing energy bands. This is done by the requirement that at least one of the eigenvalues of that matrix goes through zero. In fact that condition comes out from analyzing not the full GF in (10) but only from its second part. To circumvent this problem, we want the first term in Eq.(10) to vanish at the boundary radial points. It can be done by re-normalizing the regular solution as

$$\xi(E, r) = Z(E, r) Z^{-1}(E, S) \quad (30)$$

and accordingly the irregular solution

$$\zeta(E, r) = J(E, r) Z^T(E, S) - Z(E, r) j(\sqrt{E}S). \quad (31)$$

By direct calculations we may check that the Wronskian in matrix form defined as

$$W \{ \zeta(E, r), \xi(E, r) \}_{\nu l} = \left\{ \zeta^T(E, r) \frac{\partial}{\partial r} \xi(E, r) - \frac{\partial}{\partial r} \zeta^T(E, r) \xi(E, r) \right\}_{\nu l} \quad (32)$$

is equal to

$$W\{\zeta(E, r), \xi(E, r)\} = W\{J(E, r), Z(E, r)\} = \mathbf{1}. \quad (33)$$

Setting in (30) and (31) $r = S$ and recalling that $t^T(E) = t(E)$ it follows, that

$$\xi(E, S) = \mathbf{1} \quad \zeta(E, S) = 0. \quad (34)$$

Now, we are in position to convert GF expressed in (10) using convention (J, Z) to that in terms of (ζ, ξ) . First, we need the free GF matrix with radii on 'muffin-tin' points:

$$\begin{aligned} [g_0(E, k)]_{\nu l} &= -\frac{i}{\sqrt{E}} h_l(\sqrt{E}S) j_l(\sqrt{E}S) \delta_{\nu l} \\ &+ j_{\nu'}(\sqrt{E}S) [B(E, k)]_{\nu' l} j_l(\sqrt{E}S). \end{aligned} \quad (35)$$

Then applying the operator identity

$$[A - B]^{-1} = A^{-1} + A^{-1} [B^{-1} - A^{-1}]^{-1} A^{-1} \quad (36)$$

to the second term in (10) and replacing radial functions (J, Z) with functions (ζ, ξ) as introduced in (30) and (31) we get to the following expression of GF:

$$\langle x' | G(E, k) | x \rangle = \sum_{l_2 l_1} Y_{l_2}(\hat{x}') \langle l_2 r' | G(E, k) | l_1 r \rangle Y_{l_1}(\hat{x}) \quad (37)$$

with radial parts

$$\begin{aligned} \langle l_2 r' | G(E, k) | l_1 r \rangle &= -\sum_l [\zeta(E, r_>)]_{l_2 l} [\xi(E, r_<)]_{l l_1}^T \\ &+ \sum_{l' l} [\xi(E, r')]_{l_2 l'} [g_0^{-1}(E, k) - v_P(E)]_{l' l}^{-1} [\xi(E, r)]_{l l_1}^T. \end{aligned} \quad (38)$$

It follows from (38) that GF with radial arguments at boundary points

$$[g(E, k)]_{l_2 l_1} \equiv \langle l_2 S | G(E, k) | l_1 S \rangle \quad (39)$$

can be found from algebraic equation of Dyson type

$$g(E, k) = g_0(E, k) + g_0(E, k) v_P(E) g(E, k) \quad (40)$$

with pseudopotential amplitude $v_P(E)$ as given in (28). The poles of $g(E, k)$ are exactly the same as of the full GF $\langle x' | G(E, k) | x \rangle$ in (10), suggesting alternative way to (22) of finding energy bands

$$\det |g^{-1}(E, k)| = 0. \quad (41)$$

Searching for zeros of eigenvalues of matrix $g^{-1}(E, k)$ is much easier than that of $t^{-1}(E) - B(E, k)$ as the eigenvalue functions of the former are monotonically increasing with energy E . But some obscuring deficiency still persists as the slopes, at which these eigenvalues are crossing energy axis, are not fixed. This inconvenience can be avoided in the following way. Let us first integrate GF in the form (38) over the whole Wigner-Seitz cell

$$\begin{aligned} \int_{-a/2}^{a/2} dx \langle x | G(E, k) | x \rangle &= -\sum_l \int_{-a/2}^{a/2} dx \zeta_l(E, x) \xi_l(E, x) \\ &+ \sum_{l' l} [g(E, k)]_{l' l} \int_{-a/2}^{a/2} dx \xi_{l'}(E, x) \xi_l(E, x). \end{aligned} \quad (42)$$

Integrating the first term in (42) yields:

$$\begin{aligned} & \int_{-a/2}^{a/2} dx \zeta_{l'}(E, x) \xi_l(E, x) = \\ & \sum_{l_2 l_1} \int_0^S dr \sum_{\hat{x}} Y_{l_2}(\hat{x}) Y_{l_1}(\hat{x}) [\zeta(E, r)]_{l_2 l'} [\xi(E, r)]_{l_1 l} = \\ & \int_0^S dr [\zeta^T(E, r) \xi(E, r)]_{l' l} \end{aligned} \quad (43)$$

From the Schrödinger equation we find that radial parts $\zeta^T(E, r)$ and the energy derivative $\frac{\partial}{\partial E} \xi(E, r) \equiv \dot{\xi}(E, r)$ satisfy differential equations

$$\frac{d^2}{dr^2} \zeta^T(E, r) = \zeta^T(E, r) [v(r) - E] \quad (44)$$

and

$$\frac{\partial^2}{\partial r^2} \dot{\xi}(E, r) = [v(r) - E] \dot{\xi}(E, r) - \xi(E, r) \quad (45)$$

respectively. Multiplying (44) to the right by $\xi(E, r)$, then (45) to the left by $\zeta^T(E, r)$ and subtracting one from another, we get:

$$\int_0^S dr \zeta^T(E, r) \xi(E, r) = W \left\{ \zeta(E, r), \dot{\xi}(E, r) \right\}_{r=0} \quad (46)$$

This integral can be conventionally found if function $\psi(E, r)$ (16) is computed. From the definition of $\xi(E, r)$ in (30) it follows:

$$\xi(E, r) \psi(E, S) = \psi(E, r), \quad (47)$$

$$\dot{\xi}(E, r) \psi(E, S) + \xi(E, r) \dot{\psi}(E, S) = \dot{\psi}(E, r) = 0 \quad (r \rightarrow 0), \quad (48)$$

Inserting $\dot{\xi}(E, r)$ from (48) into (46) we get

$$\begin{aligned} & W \left\{ \zeta(E, r), \dot{\xi}(E, r) \right\}_{r=0} = \\ & W \left\{ \zeta(E, r), -\xi(E, r) \dot{\psi}(E, S) \psi^{-1}(E, S) \right\}_{r=0} = \\ & -\dot{\psi}(E, S) \psi^{-1}(E, S) \end{aligned} \quad (49)$$

Combining (46) with the result (49) we have

$$\int_0^S dr \zeta^T(E, r) \xi(E, r) = -\dot{\psi}(E, S) \psi^{-1}(E, S). \quad (50)$$

For the second integral in (42) we obtain

$$\begin{aligned} & \int_{-a/2}^{a/2} dx \xi_{l'}(E, x) \xi_l(E, x) = \int_0^S dr [\xi^T(E, r) \xi(E, r)]_{l' l} = \\ & [N_\psi(E) \psi^{-1}(E, S)]^T [N_\psi(E) \psi^{-1}(E, S)] \end{aligned} \quad (51)$$

with the definition of $N_\psi(E)$ as

$$\int_0^S dr \psi^T(E, r) \psi(E, r) = N_\psi^T(E) N_\psi(E). \quad (52)$$

With the help of (50) and (51) we may convert (42) to the form

$$\begin{aligned} \int_{-a/2}^{a/2} < x | G(E, k) | x > = \sum_l [\dot{\psi}(E, S) \psi^{-1}(E, S)]_{ll} + \\ \sum_l \{ [N_\psi(E) \psi^{-1}(E, S)] g(E, k) [N_\psi(E) \psi^{-1}(E, S)]^T \}_{ll} = \\ \sum_l P_{ll}(E, k) \end{aligned} \quad (53)$$

The left hand side of equation (53) is equal to the trace of hermitian matrix $P(E, k)$ defined as

$$P(E, k) = 1/2 [Q(E, k) + Q^\dagger(E, k)], \quad (54)$$

with

$$\begin{aligned} Q(E, k) = [\psi(E, S) N_\psi^{-1}(E)]^{-1} [\dot{\psi}(E, S) N_\psi^{-1}(E)] + \\ N_\psi(E) \psi^{-1}(E, S) g(E, k) [N_\psi(E) \psi^{-1}(E, S)]^T. \end{aligned} \quad (55)$$

The poles of the matrix $P(E, k)$ give energy bands that can be found from zeros of the determinant

$$\det |P^{-1}(E, k)| = 0. \quad (56)$$

From the analytical property of GF known in the literature as Herglotz property [10] it is expected that eigenvalues of $P^{-1}(E, k)$ -matrix must increase monotonically with energy, i.e.,

$$\frac{\partial}{\partial E} \lambda_i [P^{-1}(E, k)] \geq 0, \quad (57)$$

and with the slope equal to one if crossing energy axis.

In the formula (55) the presence of the inverse matrix $\psi^{-1}(E, S)$ may cause numerical instability if matrix $\psi(E, S)$ is singular, what may happen in practice. To avoid such complications it is convenient to combine the first and second term in Eq.(54) together with the following manipulation. First, we can compute integral in (52) using trick with energy derivative, like in (44) and (45). Then with the known procedure we get

$$\int_0^S dr \psi^T(E, r) \psi(E, r) = -W \left\{ \psi(E, r), \dot{\psi}(E, r) \right\}_{r=S}. \quad (58)$$

In equation (58) the contribution at the origin point ($r = 0$) is set to be equal zero, what is justified with normalization of $\psi(E, r)$ assumed in Eq.(16). Recalling Wronskian definition, as set in (20) and log-derivatives in (26), we may proceed with (58) getting

$$\int_0^S dr \psi^T(E, r) \psi(E, r) = \psi^T(E, S) \left\{ D_\psi(E) - D_{\dot{\psi}}(E) \right\} \dot{\psi}(E, S) \quad (59)$$

From (59) and (52) it follows the equality

$$[\psi(E, S)N_\psi^{-1}(E)]^T \left\{ D_\psi(E) - D_{\dot{\psi}}(E) \right\} [\dot{\psi}(E, S)N_\psi^{-1}(E)] = 1, \quad (60)$$

useful in converting (55) to the desired form as follows

$$Q(E, k) = [\psi(E, S)N_\psi(E)]^{-1} \times \left\{ \dot{\psi}(E, S)N_\psi^{-1}(E) + g(E, k)[\psi(E, S)N_\psi^{-1}(E)]^{-1^T} \right\} \quad (61)$$

From (61) with the help of equality (60) we may proceed to

$$Q(E, k) = [\psi(E, S)N_\psi(E)]^{-1} \times \left\{ [D_\psi(E) - D_{\dot{\psi}}(E)]^{-1} + g(E, k) \right\} [\psi(E, S)N_\psi^{-1}(E)]^{-1^T}. \quad (62)$$

But recalling $g(E, k)$ as given in (40) we get

$$[D_\psi(E) - D_{\dot{\psi}}(E)]^{-1} + g(E, k) = [g_0^{-1}(E, k) + D_0(E) - D_\psi(E)]^{-1} [g_0^{-1}(E, k) + D_0(E) - D_{\dot{\psi}}(E)] \times [D_\psi(E) - D_{\dot{\psi}}(E)]^{-1}. \quad (63)$$

that if inserted in (62) gives

$$Q(E, k) = \left\{ \psi(E, S)N_\psi^{-1}(E) + g_0(E, k)[D_0(E) - D_\psi(E)]\psi(E, S)N_\psi^{-1}(E) \right\}^{-1} \times \left\{ \dot{\psi}(E, S)N_\psi^{-1}(E) + g_0(E, k)[D_0(E) - D_{\dot{\psi}}(E)]\dot{\psi}(E, S)N_\psi^{-1}(E) \right\}. \quad (64)$$

With the Wronskian definition as in (20) last expression can be simplified further

$$Q(E, k) = N_\psi(E) \left\{ \psi(E, S) + C(E, k)W^T[\psi, j] \right\}^{-1} \times \left\{ \dot{\psi}(E, S) + C(E, k)W^T[\dot{\psi}, j] \right\} N_\psi^{-1}(E) \quad (65)$$

with the matrix $C(E, k)$ formed from KKR structure functions $B(E, k)$:

$$[C(E, k)]_{l'l} = -\frac{i}{\sqrt{E}} h_{l'}(\sqrt{E}S)\delta_{l'l} + j_{l'}(\sqrt{E}S)[B(E, k)]_{l'l} \quad (66)$$

These two last equations give the most convenient way to construct the novel KKR-matrix $P(E, k)$ with desired properties of the eigenvalues.

4. Generalised Lloyd formula

The Lloyd formula is often used to calculate the number of states for a 'muffin-tin' model potential. We derive it here in the form similar to that used in the paper by Kaprzyk and Bansil [6].

It is well known that the total number of states $N(E)$ is done as

$$N(E) = -\frac{1}{\pi} \text{Im} \int_{-\infty}^E dE \sum_{k \in BZ} \int_{(WS)} dx < x | G(E, k) | x >. \quad (67)$$

We show that the space integral in (67) can be expressed as a perfect energy derivative and the energy integration can be done explicitly. We start with (53) putting it in the form

$$\int_{-a/2}^{a/2} dx \langle x | G(E, k) | x \rangle = \text{Tr} \{ \psi^{-1}(E, S) \dot{\psi}(E, S) \} + \quad (68)$$

$$\text{Tr} \{ g(E, k) [N_\psi(E) \psi^{-1}(E, S)]^T [N_\psi(E) \psi^{-1}(E, S)] \},$$

then with the help of (59) we find (at $r = S$)

$$N_\psi^T(E) N_\psi(E) = -\psi^T(E, S) \dot{\psi}(E, S) \psi(E, S). \quad (69)$$

With the last result, (68) can be written as

$$\int_{-a/2}^{a/2} dx \langle x | G(E, k) | x \rangle = \quad (70)$$

$$\text{Tr} \left\{ \psi^{-1}(E, S) \dot{\psi}(E, S) \right\} - \text{Tr} \left\{ g(E, k) \dot{\psi}(E, S) \right\}.$$

The last step consists of proving the equality

$$\frac{\partial}{\partial E} g(E, k) = g(E, k) \dot{\psi}(E, S) g(E, k) \quad (71)$$

which if inserted into (70) gives the result

$$\int_{-a/2}^{a/2} dx \langle x | G(E, k) | x \rangle = -\frac{\partial}{\partial E} \text{Tr} \ln [g(E, k) \psi^{-1}(E, S)]. \quad (72)$$

The algebraic equality (71) is a consequence of GF properties stating that

$$\frac{\partial}{\partial E} G(E) = -G(E) G(E). \quad (73)$$

If applied to our Bloch-Fourier GF with radial arguments on 'muffin-tin' boundary points we get

$$\begin{aligned} & \langle \hat{x}_2 S | \frac{\partial}{\partial E} G(E, k) | \hat{x}_1 S \rangle = \\ & - \int_{-a/2}^{a/2} dx \langle \hat{x}_2 S | G(E, k) | x \rangle \langle x | G(E, k) | \hat{x}_1 S \rangle \end{aligned} \quad (74)$$

and for the radial part defined in (37)

$$\begin{aligned} & \langle l_2 S | \frac{\partial}{\partial E} G(E, k) | l_1 S \rangle = \\ & - \int_0^S dr \langle l_2 S | G(E, k) | l r \rangle \langle l r | G(E, k) | l_1 S \rangle. \end{aligned} \quad (75)$$

Inserting proper radial arguments into (75) we get according to (36) and (34) that

$$\langle l_2 S | G(E, k) | l r \rangle = [g(E, k) \zeta^T(E, r)]_{l_2 l}, \quad (76)$$

$$\langle l S | G(E, k) | l_1 r \rangle = [\xi(E, r) g(E, k)]_{l l_1}, \quad (77)$$

which allow us to rewrite (75) in the form

$$\frac{\partial}{\partial E} [g(E, k)] = -g(E, k) \left[\int_0^S dr \xi^T(E, r) \xi(E, r) \right] g(E, k). \quad (78)$$

Computing integral in (78) can be done with the help of (69) and leads to the result

$$\int_0^S dr \xi^T(E, r) \xi(E, r) = -\dot{D}_\xi(E) = -\dot{D}_\psi(E). \quad (79)$$

Inserting this relation into (78) proves validity of (71). The total number of states seen in (67) can now be found from

$$N(E) = \frac{1}{\pi} \text{Im} \ln(\det |\psi(E, S)|) - \frac{1}{\pi} \sum_{k \in \text{BZ}} \text{Im} \ln \det |g(E, k)|. \quad (80)$$

In passing from (72) to (80) we used algebraic equality

$$\text{Tr} \ln[A] = \ln[\det |A|]. \quad (81)$$

In (80) the first term accounts for the number of nodes on regular solution from origin up to radius S , and the second term comes out from the Bloch states at each of k -points in BZ.

5. Results

In order to illustrate numerically how the novel approach to KKR method works compared to standard one, we have performed calculations for the 1D Mathieu potential of the form

$$v(x) = -U_0 \cos(2\pi x/a), \quad (82)$$

and used lattice constant $a = 3.0$ a.u. and $U_0 = 5$ Ry (see Fig. 1). In Fig. 2 we show eigenvalue functions as calculated using both standard and novel method (Eqs. (22) and (56)) for the potential (82). One can see that zeros of the eigenvalue functions are exactly the same. In the novel method case we can find them numerically very easily but in the standard KKR approach it is much more difficult. Moreover, to illustrate how the eigenvalue curves behave when the number of atoms in the unit cell grows, we performed the calculations in two cases. In the first case we put only one atom in the unit cell with the 'muffin-tin' radius $S = 1.5$ a.u. and the symmetric potential given by (82). In the second case we divided the unit cell into four 'muffin-tin' segments of the same length and touching each other, but without changing the total potential in the unit cell. So, in this case the potential in each segment is not symmetrical, but the physical situation is exactly the same. What changed is the size of resulting matrices and hence number of the eigenvalue functions. These functions in both cases are shown in Fig. 3 for the wave vector $k = 0.6\pi/a$. Note that in the second case the lines are not derived from interpolation but simply connect calculated points, which are not shown in Fig. 3.

Now all the benefits of the novel method can be underlined. First, we observe that the eigenvalue functions do not cross each other and grow monotonically. Moreover, they form almost straight lines with the slope of unity when passing through zero. Secondly, we can see that with the increasing number of atoms in the unit cell the eigenvalue curves become straight for the wider range of energies. So, in the limit of infinite number of atoms in the unit cell, the method seems to become linear. This makes the method not very sensitive to the number of energy points used in the interpolation procedure, when finding zeros of eigenvalue curves. This last advantage opens possibilities of calculation of very complex systems, even with hundreds atoms in the unit cell in reasonable time without losing accuracy.

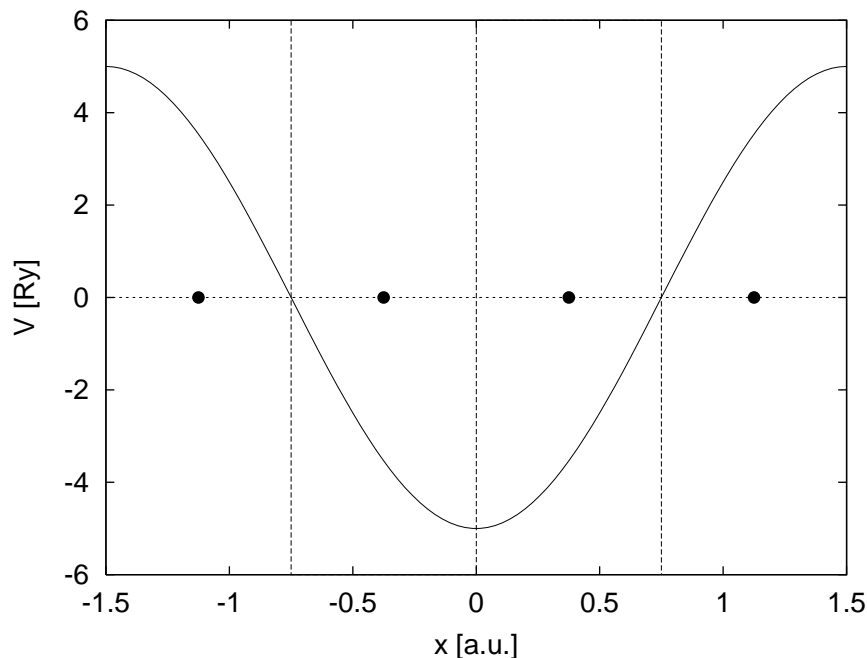


Figure 1. Mathieu potential used in calculations. The black dots denote four atoms in the unit cell case. In the case of one atom, it is placed in the middle of the unit cell.

6. Summary

In this paper we have reformulated one-dimensional full potential KKR formalism. Then we have derived novel form of the KKR secular matrix. To exclude first term in the full Green function we have normalized solutions of the Schrödinger equation in such a way that the 'irregular' solution disappears at boundary points of 'muffin-tin' segments. Then by integrating the full Green function over the Wigner-Seitz cell we have derived the final result, that is the expressions for the secular matrix $P(E, k)$ as well as for the generalised Lloyd formula. The eigenvalues of the inverse matrix $P^{-1}(E, k)$ increase monotonically with energy and almost linearly for every k -point. In the case of increasing number of atoms in the unit cell the eigenvalue functions become more linear.

Finally, we performed numerical calculations for the case of the Mathieu potential. The results show that the zeros of the eigenvalues can be easily found, even for very complex systems, without any loss of accuracy. This formalism can be extended to the higher-dimensional systems with the minor changes.

Appendix

In this appendix we briefly generalise the formalism introduced in sections 2, 3 and 4 for many atoms in the unit cell. In this case one has to solve the Schrödinger equation

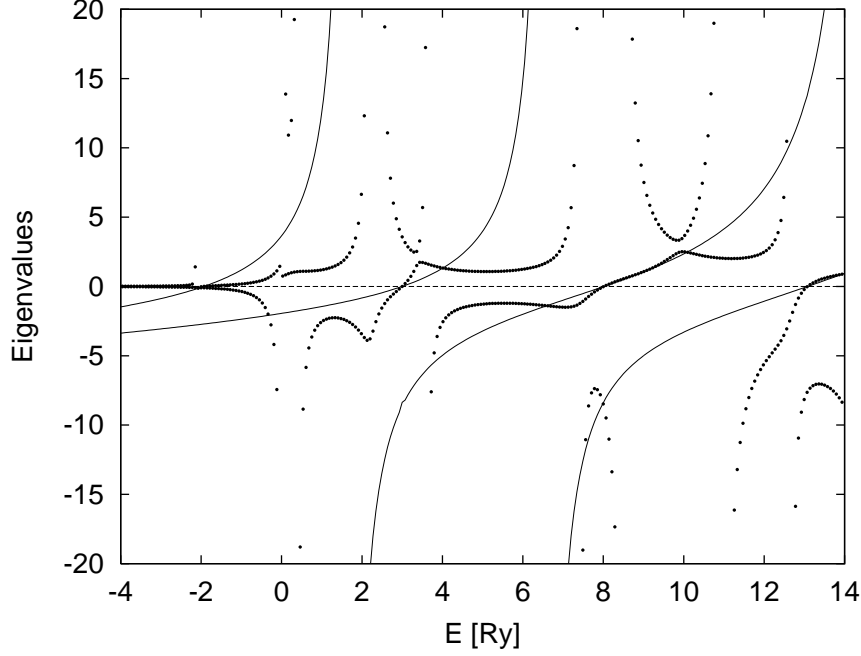


Figure 2. Comparison of the standard KKR method (dots) and the novel one (solid lines) as applied to the Mathieu potential (82). The wave vector is $k = 0.6\pi/a$.

with the potential

$$V(x) = \sum_{n=-\infty}^{\infty} \sum_{\alpha=1}^p v_{\alpha}(x - na - a_{\alpha}), \quad (\text{A.1})$$

where a_{α} is the position of α -th atom in the unit cell with p equal to the number of atoms in the unit cell. At each 'muffin-tin' atomic segment we solve Schrödinger equation starting at origin from

$$[\psi^{\alpha}(E, r)]_{l'l} = r^l \delta_{l'l} \quad r \rightarrow 0. \quad (\text{A.2})$$

The resulting ψ matrix has the form

$$[\psi(E, r)]_{\alpha'l', \alpha l} = [\psi^{\alpha}(E, r)]_{l'l} \delta_{\alpha\alpha'} \quad (\text{A.3})$$

with the size $2p \times 2p$. Similarly we construct all other matrices introduced in the previous sections. GF in (ζ, ξ) representation now has a form:

$$\begin{aligned} & \langle x' + a_{\alpha'} | G(E, k) | x + a_{\alpha} \rangle = \\ & - \sum_l \zeta_l^{\alpha}(E, x_{>}) \xi_l^{\alpha}(E, x_{<}) \delta_{\alpha\alpha'} \\ & + \sum_{l, l'} \xi_{l'}^{\alpha'}(E, x') [g_0^{-1}(E, k) - v_P(E)]_{\alpha'l', \alpha l}^{-1} \xi_l^{\alpha}(E, x). \end{aligned} \quad (\text{A.4})$$

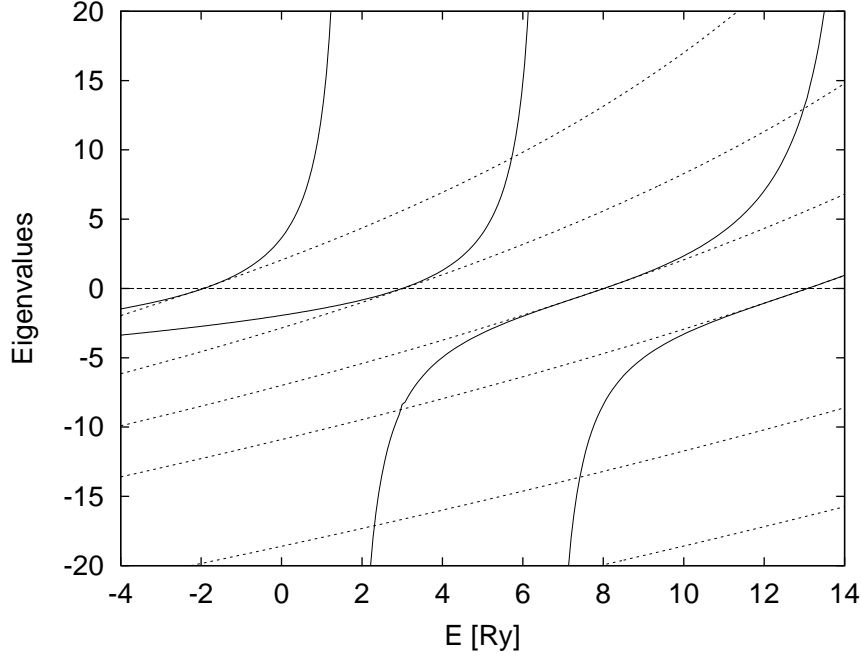


Figure 3. The eigenvalue functions for the Mathieu potential (82) and the wave vector $k = 0.6\pi/a$. The case with one and four atoms in the unit cell is represented by solid and dashed lines, respectively.

The structure constants in this generalised case can be given explicitly with the matrix elements $[B(E, k)]_{\alpha'l', \alpha l}$:

$$[B(E, k)]_{\alpha 0, \alpha' 0} = [B(E, k)]_{\alpha 1, \alpha' 1} = \frac{\exp(i\sqrt{E}a) \cos \sqrt{E}a_{\alpha\alpha'} - \cos(ka - \sqrt{E}a_{\alpha\alpha'})}{i\sqrt{E}[\cos ka - \cos \sqrt{E}a]} \quad (\text{A.5})$$

$$+ \frac{1}{i\sqrt{E}} \exp(i\sqrt{E}|a_{\alpha\alpha'}|)(1 - \delta_{\alpha\alpha'}),$$

$$[B(E, k)]_{\alpha 1, \alpha' 0} = [B(E, k)]_{\alpha' 0, \alpha 1}^* = \frac{\exp(i\sqrt{E}a) \sin \sqrt{E}a_{\alpha\alpha'} + \sin(ka - \sqrt{E}a_{\alpha\alpha'})}{i\sqrt{E}[\cos ka - \cos \sqrt{E}a]} \quad (\text{A.6})$$

$$+ \frac{1}{\sqrt{E}} \exp(i\sqrt{E}|a_{\alpha\alpha'}|) \text{sgn}(-a_{\alpha\alpha'})(1 - \delta_{\alpha\alpha'}),$$

with $a_{\alpha\alpha'} = a_\alpha - a_{\alpha'}$. Finally we define the matrix $P(E, k)$ by the relation:

$$\sum_{\alpha} \int_{-S_{\alpha}}^{S_{\alpha}} dx \langle x + a_{\alpha} | G(E, k) | x + a_{\alpha} \rangle = \text{Tr}[P(E, k)] \quad (\text{A.7})$$

with S_α being muffin-tin radius of the α -th atom. Following the steps described in previous sections we find, that the matrix $P(E, k)$ can be found using Eqs. (54) and (55) by adding atomic indexes to the matrix elements, as it is done for structure constants matrix $B(E, k)$. The band structure is still determined by the relation (56).

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